PROCESS FOR THE CATALYTIC SELECTIVE OXIDATION OF SULFUR COMPOUNDS

Field of the invention

The present invention relates to a process for the catalytic selective oxidation of sulfur compounds in a hydrocarbonaceous feedstock to sulfur dioxide.

Background of the invention

Hydrocarbonaceous feedstock are usually desulfurised in a hydrodesulfurisation process. In this process, the sulfur containing feedstock is contacted with a hydrodesulfurisation catalyst, typically a Co-Mo or Ni-Mo catalyst, in the presence of hydrogen, at elevated temperature and pressure. Hydrodesulfurised hydrocarbonaceous streams still contain sulfur compounds, in particular sulfur compounds that are difficult to remove such as heterocyclic sulfur compounds like thiophenes, benzothiophenes, substituted and condensed ring dibenzothiophenes.

Catalysts containing nickel, zinc oxide and alumina may be used for deep desulfurisation of hydrocarbon streams in the presence of hydrogen. These catalysts are able to remove "difficult" sulfur compounds and to achieve sulfur concentrations as low as 0.1 ppm. In WO 01/15804, for example, a catalyst is disclosed having 5-25 wt% Ni, 30-70 wt% ZnO and the remainder alumina. The catalyst of WO 01/15804 has a double function: nickel catalyses the reaction of sulfur with hydrogen to form hydrogen sulphide and zinc oxide absorbs the hydrogen sulphide formed.

Hydrocarbonaceous streams may also be desulfurized by oxidising the sulfur of the sulfur

compounds to sulfur dioxide in a vapour phase
process. US 2,640,010, for example, describes the
oxidation of sulfur compounds like hydrogen sulphide,
mercaptans and disulphides in petroleum hydrocarbons
to sulfur dioxide, by passing the vapour of the
hydrocarbon over an oxidation catalyst comprising
cuprous sulphide. US 2,361,651 describes a process
for sweetening and desulfurising sour hydrocarbon
distillates by contacting vapours of said distillates
in the presence of oxygen with a catalyst comprising
copper oxide. The reaction involved in the process is
an oxidation of mercaptans, sulfides and disulfides
to sulfur dioxide by the action of the copper
catalyst in the presence of oxygen.

A disadvantage of the processes disclosed in
US 2,640,010 and US 2,361,651 is that "difficult"
sulfur compounds like thiophenes are not removed.

Summary of the Invention

A process for the catalytic selective oxidation
of sulfur compounds in a hydrocarbonaceous feedstock
to sulfur dioxide is provided, comprising the steps
of:
contacting a gaseous feed mixture of the
hydrocarbonaceous feedstock and a molecular-oxygen
containing gas with a catalyst at a temperature of at
most 500 °C, said catalyst comprising a group VIII
noble metal on a catalyst carrier, said feed mixture
having oxygen-to-carbon ratio of below 0.15.

Further, a process for the desulfurization of a
hydrocarbonacous feedstock is provided, comprising
the steps of:
contacting a gaseous feed mixture of the
hydrocarbonaceous feedstock and a molecular-oxygen
containing gas with a catalyst at a temperature of at

most 500 °C, said catalyst comprising a group VIII
noble metal on a catalyst carrier, said feed mixture
having oxygen-to-carbon ratio of below 0.15, thereby
selectively oxidizing sulfur compounds in the
hydrocarbonaceous feedstock to sulfur dioxide; and
removing the thus-formed sulfur dioxide from the
hydrocarbonaceous feedstock.

Detailed description of the invention

It has now been found that the sulfur from
"difficult" sulfur compounds like thiophenes in
hydrocarbonaceous streams can be converted into
sulfur dioxide by catalytic selective oxidation by
using a catalyst comprising a Group VIII noble metal.
The thus-formed sulfur dioxide can be removed by
processes known in the art. Reference herein to
selective oxidation of sulfur compounds is to the
oxidation of sulfur compounds with no or minimal
oxidation of the non-sulfur containing
hydrocarbonaceous compounds.

An advantage of selective oxidation followed by
removal of sulfur dioxide is that no hydrogen is
needed for the desulfurisation. Another advantage of
the vapour phase selective oxidation process is that
the process can be performed at ambient pressure.
Moreover, with the process according to the invention
it is possible to achieve deep desulfurisation
without using nickel-containing catalysts.

Accordingly, the present invention relates to a
process for the catalytic selective oxidation of
sulfur compounds in a hydrocarbonaceous feedstock to
sulfur dioxide, wherein a gaseous feed mixture of the
hydrocarbonaceous feedstock and a molecular-oxygen
containing gas is contacted with a catalyst at a
temperature of at most 500 °C, the catalyst

comprising a group VIII noble metal on a catalyst carrier, wherein the oxygen-to-carbon ratio of the feed mixture is below 0.15.

Sulfur compounds that can be selectively oxidised by the process according to the invention are for example hydrogen sulphide, mercaptans, disulphides, or heterocyclic sulfur compounds such as thiophenes, benzothiophenes, or substituted and condensed ring dibenzothiophenes.

The hydrocarbonaceous feedstock is a hydrocarbonaceous feedstock that is gaseous under the conditions prevailing at the catalyst surface. Preferred feedstocks are feedstocks that are gaseous at standard temperature and pressure (STP; 0 °C, 1 atm.) conditions such as methane, natural gas, LPG and other gaseous hydrocarbon streams. Further, feedstocks that are liquid under STP conditions but gaseous at the conditions prevailing at the catalyst surface such as naphtha, diesel or gasoline are suitable feedstocks.

The catalyst of the process according to the invention comprises as catalyst carrier an oxidising solid surface, typically in the form of solid particles. Reference herein to an oxidising surface is to a surface that is able to activate molecular oxygen. Preferably, the catalyst carrier comprises a refractory oxide. Refractory oxides such as stabilised and partially stabilised zirconia, ceria, yttria, silica, alumina, titania and combinations thereof are particularly suitable. A catalyst carrier comprising stabilised or partially stabilised zirconia is most preferred.

Alternatively, the catalyst carrier may comprise a non-refractory oxide bulk material having an

oxidising surface. Examples of such materials are a Fe, Cr and Al containing alloy (commercialised as FECRALLOY) with an alumina or zirconia surface layer (FECRALLOY is a trademark).

The catalyst comprises one or more catalytically active metals supported on the solid surface or carrier. These catalytically active metals are Group VIII noble metals, more preferably platinum, rhodium, iridium or a combination of two or more thereof.

Typically, the catalyst comprises the catalytically active metal(s) in a concentration in the range of from 0.02 to 10% by weight, based on the total weight of the catalyst, preferably in the range of from 0.1 to 5% by weight. The catalyst may further comprise a performance-enhancing inorganic metal cation selected from Al, Mg, Zr, Ti, La, Hf, Si, Ba, and Ce which is present in intimate association supported on or with the catalytically active metal, preferably a zirconium and/or cerium cation.

Catalysts comprising a noble metal on a carrier are also suitable for the catalytic partial oxidation of hydrocarbons, typical at temperatures above 700 °C. It has been found that at much lower temperatures, typically between 200 and 500 °C, the oxidation of sulfur compounds takes preferentially place as compared to the oxidation of hydrocarbons.

In order to prevent degradation of hydrocarbon compounds, the process temperature is maintained at at most 500 °C. Preferably, the process temperature is in the range of from 200 to 500 °C, more preferably of from 200 to 300 °C.

The pressure at which the feed mixture is contacted with the catalyst is preferably in the range of from 1 to 10 bar (absolute), more preferably

of from 1 to 5 bar (absolute). Most preferably, the feed mixture is contacted with the catalyst at ambient pressure.

The molecular-oxygen containing gas may be oxygen, air or oxygen-enriched air. Preferably, air is used as molecular-oxygen containing gas.

It will be appreciated that the exact process conditions, such as the temperature at which the catalyst is maintained, pressure, gas or liquid velocity and the oxygen-to-carbon ratio in the feed mixture, will inter alia depend on the catalyst used, the required sulfur conversion and selectivity, and the boiling characteristics of the hydrocarbonaceous feedstock.
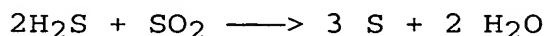
The oxygen-to-carbon ratio of the feed mixture is at most 0.15, preferably at most 0.10. Reference herein to the oxygen-to-carbon ratio is to the ratio of oxygen in the form of molecules (O_2) to carbon atoms present in the hydrocarbonaceous feedstock.

The process according to the invention is very suitable for deep desulfurisation of hydrocarbonaceous streams. It is particularly suitable for the removal of hydrogen sulphide from gaseous hydrocarbonaceous steams comprising up to 10% v/v hydrogen sulphide or the removal of "difficult" sulfur compounds from liquid hydrocarbonaceous steams comprising up to 1000 ppmw sulfur.

The sulfur dioxide formed may be removed by techniques known in the art. In liquid feedstocks, sulfur dioxide may for example be removed by distillation or stripping. Suitable techniques known in the art for the removal of sulfur dioxide from gaseous feedstocks are for example solvent extraction using an aqueous amine solution or an alkaline

solution, absorption on copper, barium or cerium oxide, or reaction with lime to produce gypsum.

In order to remove larger amounts of hydrogen sulphide from gaseous hydrocarbonaceous feedstocks, the selective oxidation process according to the invention can suitably be applied in combination with a process for the conversion of H_2S/SO_2 mixtures into elemental sulfur according to the well-known Claus reaction:

$$2H_2S + SO_2 \longrightarrow 3\ S + 2\ H_2O$$

Part of the hydrogen sulphide, preferably about one third of the total volumetric amount of hydrogen sulphide, is then converted into sulfur dioxide by the catalytic selective oxidation process according to the invention.

The process according to the invention will be further illustrated by the following non-limiting examples.

EXAMPLE 1

Catalyst preparation

Catalyst 1

Particles (1 mm average diameter) of zirconia partially stabilised with yttria (Y-PSZ) were coated with a zirconia paint (zirconium oxide partially-stabilised with 4 %wt CaO; type ZO; ex. ZYP Coatings Inc., Oak Ridge, USA) and provided with 0.9 wt% Rh, 0.9 wt% Ir, 0.6 wt% Zr, 1.9 wt% Ce by impregnating the painted particles with a solution containing rhodium tri chloride, iridium tetra chloride, zirconyl nitrate and cerium nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

Catalyst 2 (comparative)

Particles (1 mm average diameter) of zirconia partially stabilised with yttria (Y-PSZ) were coated with a zirconia paint (see above under catalyst 1) and provided with 0.5 wt% Zr, 1.6 wt% Ce by impregnating the painted particles with a solution containing zirconyl nitrate and cerium nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

Catalyst 3

Particles (30-80 mesh) of Y-PSZ were coated with a zirconia paint (see above under catalyst 1) and provided with 1.6 wt% Rh, 1.0 wt% Zr, 1.6 wt% Ce by impregnating the painted particles with a solution containing rhodium tri chloride, zirconyl nitrate and cerium nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

Catalyst 4

Particles (30-80 mesh) of zirconia-toughened alumina partially stabilised with ceria (Ce-ZTA) were impregnated with a solution containing H_2PtCl_6 and zirconyl nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours. The resulting catalyst particles contained 5 wt% Pt and 7 wt% Zr.

Catalyst 5

Calcined (2 hours at 1000 °C) particles (30-80 mesh) of alumina stabilised with magnesium oxide were provided with 0.6 wt% Ir by impregnating the particles with a iridium tetra chloride containing solution. The impregnated particles were dried (2 hours at 120 °C) and calcined (2 hours at 700 °C).

Catalyst 6

Particles (1 mm average diameter) Y-PSZ were coated with a zirconia paint and provided with 0.8 wt% Rh, 0.8 wt% Ir, 0.6 wt% Zr, 1.7 wt% Ce by impregnating the painted particles with a solution containing rhodium tri chloride, iridium tetra chloride, zirconyl nitrate and cerium nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

Catalytic selective oxidation

Approximately 1 g of catalyst particles were loaded in a 6 mm inner diameter reactor tube. A gas mixture of air and H_2S-containing methane was passed over the catalyst particles at elevated temperature and at ambient pressure.

In Table 1, the H_2S concentration of the H_2S-containing methane, the oxygen-to-carbon ratio of the air/methane mixture, the gas space velocity (Nl feed mixture per kg catalyst per hour), the temperature at which the catalyst is maintained, the H_2S conversion and the selectivity are given for each catalyst. The selectivity is calculated as the quotient of the molar SO_2/CO_2 ratio in the effluent and the S/C ratio in the feed.

It can be seen from the results in Table 1 that very high H_2S conversions are obtained when the methane feed is oxidised over a catalyst comprising Pt, Rh and/or Ir (catalysts 1, 3-6). When a catalyst without catalytically active metal is used (catalyst 2), the temperature has to be increased above 500 °C in order to achieve such a high conversion.

Table 1 Selective oxidation of H_2S in methane: feed composition, process conditions and results.

Catalyst No.	1		2 (comparison)		3	4	5	6
H_2S (% v/v)	2.8	2.0	2.5.	2.5	2.0	1.7	1.5	1.6
O_2:C	0.06	0.04	0.05	0.05	0.05	0.07	0.05	0.06
GSV (Nl/kg/h)	7,000	7,000	7,000	7,000	7,000	7,000	13,000	7,000
T (°C)	360	459	413	553	470	458	467	433
H_2S conversion (%)	99.9	99.7	73.7	99.9	97.1	94.7	95.2	96.7
selectivity	222	373	5070	8400	53	57	57	57

- 10 -

EXAMPLE 2

0.95 g of particles of catalyst 1 were loaded in a 6 mm inner diameter reactor tube. A gas mixture of air and thiophene-containing methane was passed over the catalyst particles at elevated temperature and ambient pressure. Two different experiments with different feed composition and different process conditions were carried out.

In Table 2, the sulfur concentration of the methane, the oxygen-to-carbon ratio of the air/methane mixture, the gas space velocity (Nl feed mixture per kg catalyst per hour), the temperature at which the catalyst is maintained, the thiophene conversion and the selectivity are given for the two experiments. The selectivity is calculated as the quotient of the molar SO_2/CO_2 ratio in the effluent and the S/C ratio in the feed.

Table 2   Selective oxidation of thiophene in methane: feed composition, process conditions and results.

experiment	a	b
ppmw S	11,400	300
O_2:C	0.05	0.02
GSV (Nl/kg/h)	8,000	7,000
T (°C)	391	304
thiophenes conversion (%)	99.8	79.9
selectivity	28	1816

EXAMPLE 3

0.94 g of particles of catalyst 1 were loaded in a 6 mm inner diameter reactor tube. A mixture of air and thiophene-containing naphtha was passed over the catalyst particles at a temperature of 320 °C and

ambient pressure. The naphtha had a boiling range of 40-180 °C, a H/C ratio of 1.8, a density of 0.74 g/ml.

In Table 3, the sulfur concentration of the naphtha, the oxygen-to-carbon ratio of the air/naphtha mixture, the liquid space velocity (kg naphtha per kg catalyst per hour), the temperature at which the catalyst is maintained, the thiophene conversion and the selectivity are given. The selectivity is calculated as the quotient of the molar SO_2/CO_2 ratio in the effluent and the S/C ratio in the feed.

Table 3 Selective oxidation of thiophene in naphtha: feed composition, process conditions and results.

ppmw S	590
O_2:C	0.003
LSV (kg/kg/h)	23.4
T (°C)	320
thiophenes conversion (%)	62.7
Selectivity	428

EXAMPLE 4

Catalyst preparation

Catalyst 7

Particles (30-80 mesh average diameter) of zirconia partially stabilised with yttria (Y-PSZ) were coated with a zirconia paint (zirconium oxide partially-stabilised with 4 %wt CaO; type ZO; ex. ZYP Coatings Inc., Oak Ridge, USA) and provided with 2.26 wt% Ir, 0.98 wt% Zr, 1.56 wt% Ce by impregnating the painted particles with a solution containing iridium tetra chloride, zirconyl nitrate and cerium nitrate.

The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

Catalytic selective oxidation

2.04 g of particles of catalyst 7 were diluted with 2.13 g SiC (0.05 mm) to improve heat transfer and flow properties and loaded in a 15 mm inner diameter reactor tube. A gas mixture of air and thiophene-containing methane was passed over the catalyst particles at elevated temperature and ambient pressure. Three different experiments with the same feed composition and different temperatures were carried out. The sulfur content of the feed was 210 ppmv thiophene. The O_2/C ratio was 0.005 and the GHSV 2500 Nl/kg/hr.

In Table 4, the thiophene conversion and selectivity are given for the three experiments. The selectivity is calculated as the quotient of the molar SO_2/CO_2 ratio in the effluent and the S/C ratio in the feed.

Table 4   Selective oxidation of thiophene in methane

experiment	a	b	c
temperature (°C)	220	250	300
thiophenes conversion (%)	99.8	99.8	99.8
selectivity	2380	1590	676

EXAMPLE 5

2.03 g of particles of catalyst 7 were diluted with 2.2 g SiC (0.05 mm) to improve heat transfer and flow properties and loaded in a 15 mm inner diameter reactor tube. A gas mixture of air and LPG (5.9% v/v butane, balance propane) containing 50 ppmv each of

H_2S, COS, ethyl mercaptan, tetrahydrothiophene and diethyl disulfide was passed over the catalyst particles at elevated temperature and ambient pressure. The O_2/C ratio was 0.002 and the GHSV 3600 Nl/kg/hr.

In Table 5, the conversion of each of the sulfur species is given for a reactor temperature of 275 °C.

Table 5   Conversion of different sulfur species in LPG

sulfur species	conversion (%)
H_2S	99.97
COS	99.9
ethyl mercaptan	99.97
tetrahydrothiophene	97
diethyl disulfide	99.9

The selectivity (calculated as the quotient of the molar SO_2/CO_2 ratio in the effluent and the total S/C ratio in the feed) was 65.

EXAMPLE 6

Catalyst preparation

Catalyst 8

Particles (20-30 mesh average diameter) of zirconia partially stabilised with yttria (Y-PSZ) were coated with a zirconia paint (zirconium oxide partially-stabilised with 4 %wt CaO; type ZO; ex. ZYP Coatings Inc., Oak Ridge, USA) and provided with 0.81 wt% Rh, 0.78 wt% Ir, 0.98 wt% Zr, 1.57 wt% Ce by impregnating the painted particles with a solution containing rhodium tri chloride, iridium tetra chloride, zirconyl nitrate and cerium nitrate. The

impregnated particles were dried at 140 °C during 2
hours and calcined at 700 °C during 2 hours.

Catalytic selective oxidation

5   1.93 g of particles of catalyst 8 were mixed with
1.81 gram SiC (0.05 mm) and loaded in a 15 mm inner
diameter reactor tube. A mixture of air and a
hydrocracked naphtha (ex Pernis refinery, initial
boiling point 91 °C, final boiling point 195 °C,
containing a total of 32 ppmw S, predominantly as

10   (substituted) thiophenes, sulphides and disulfides)
was passed over the catalyst particles at two
different temperatures, 250 and 270 °C, an O_2/C ratio
of 0.003 and a liquid space velocity of 3.5 kg/kg/hr.

In Table 6, the sulfur conversion of the naphtha,

15   and the selectivity are given. The conversion is
based on the S analysis of the liquid product. The
selectivity is calculated as the quotient of the
molar SO_2/CO_2 ratio in the effluent and the S/C ratio
in the feed.

Table 6   Selective oxidation of sulfur species in
naphtha

experiment	a	b
temperature (°C)	250	270
S conversion (%)	88	92
selectivity	334	17